

# Thermal stability of lithium-rich manganese-based cathode



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0.5Li<sub>4/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>–0.5LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>

## ABSTRACT

Thermal stability of a lithium-rich layered oxide cathode material with composition 0.5Li<sub>4/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>–0.5LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (LMO–NCM) is investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Investigated material shows higher thermal stability (higher onset temperature) than LiCoO<sub>2</sub>. The state of charge and previous cycling history of LMO–NCM, particularly activation of lithium manganese oxide (LMO) “component” during first charge, affect its thermal stability. Activation of LMO has an ambivalent effect on cathode thermal stability: on the one hand, the onset temperature of cathode decomposition is increased, probably due to the change in oxidation states of Ni, Co and Mn after the first cycle. On the other hand, the enthalpy of decomposition increases, presumably due to formation of unstable oxygen in the lattice. X-ray diffraction (XRD) analyses of cathodes before and after thermal decomposition at 600 °C indicate differences in decomposition reactions of charged cathodes, depending on state of charge and cycling history.

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## 1. Introduction

In lithium-ion battery, cathodes are usually considered as a limiting factor for efficient energy storage [1]. Most common cathode materials have low specific capacity, which equals approximately 130 to 150 mAh g<sup>−1</sup> for layered oxides LiCoO<sub>2</sub> (LCO) and Li[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]O<sub>2</sub> (NCM), and 170 mAh g<sup>−1</sup> for LiFePO<sub>4</sub> (LFP) [2]. LCO is still the most commonly used cathode material for portable electronics due to its good balance between capacity, rate capability and ease of processing [3]. However, with increasing emphasis on safety of large-scale batteries, there is a need to develop alternative cathode materials with good thermal stability. Layered oxides LCO and NCM tend to decompose at higher temperatures, and the decomposition generates gaseous oxygen, which reacts with electrolyte, leading to thermal runaway of the cell [4]. Olivine LFP with good thermal stability has been proposed as a candidate to replace the layered oxides. However, it has a low packing density and it operates at low voltage, which leads to low energy density at cell level [3].

Lithium-rich layered oxides from the family xLi<sub>2</sub>MnO<sub>3</sub>–(1 – x)LiMO<sub>2</sub> (M = Ni, Co, Mn), also known as LMO–NCM, have drawn much attention

recently and are considered as alternative cathode materials [5]. Their advantages are high discharge capacity of more than 200 mAh g<sup>−1</sup> [6], and lower price due to lower Co content. On the other hand, main drawbacks of these materials are continuous voltage fade upon cycling, high irreversible capacity in first cycle and poor rate capability [5].

One special feature of these lithium-rich layered oxides is the characteristic charge profile during the first cycle that is different from that in the second cycle. Lithium is extracted separately from both components in the first cycle, resulting in two regions in the first charge curve: a first region up to 4.4 V where the NCM component is de-lithiated (i.e. increase in oxidation states of Ni and Co) and a second region above 4.4 V where the LMO component is activated [5]. Previous XANES experiments have suggested that the oxidation state of manganese in Li<sub>2</sub>MnO<sub>3</sub> remains 4+ during charging, so the Li extraction is compensated by oxygen oxidation or oxygen gas release [6,7]. Phenomenologically, during discharge, most of the capacities can be accounted for by the reduction of Ni, Co and Mn transition metals in the material, with lithiation of the NCM component first above ~3.8 V and afterwards LMO below that. Thus, during the second charge, Li will be extracted first from the LMO component and then from the NCM component, resulting in a different charge profile as the first charge. We will show in the study that the difference in the first and second cycle charge mechanisms affects its thermal stability.

Recent research using differential electrochemical mass spectroscopy (DEMS) has confirmed O<sub>2</sub> gas release during first charge [8]. Further research suggests O<sub>2</sub> is released from the surface of the particles at the beginning of LMO activation plateau and oxygen is oxidized with

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structure densification in the bulk at the end of the charging process [9, 10]. Oxygen release and formation of unstable oxygen in the crystal structure of the active material raise additional concerns regarding material's safety.

This research aims to study the thermal stability of LMO–NCM based cathode and to compare it with conventional cathode materials such as LCO and NCM. Thermal stability of LMO–NCM is investigated as a function of state of charge (Li content) and cycling history. The influence of the LMO activation step (oxygen oxidation or gas emission) on thermal stability of material will be discussed.

## 2. Experimental

The active material was provided by Samsung SDI, Korea with a composition of  $0.5\text{Li}_{4/3}\text{Mn}_{2/3}\text{O}_2-0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (equivalent to  $\text{Li}_{1.167}\text{Mn}_{0.5}\text{Ni}_{0.167}\text{Co}_{0.167}\text{O}_2$ ). Cathode slurry, composed of 80% active material, 10% acetylene black (AB; 50% compressed 99.9% metals basis, Alfa Aesar) and 10% polyvinylidene difluoride (PVDF, HSV900, Kynar) as 6% solution in N-Methyl-2-pyrrolidone (NMP; ACS reagent  $\geq 99.0\%$ , Sigma-Aldrich) was prepared and homogenized in a mortar and coated on a  $15\ \mu\text{m}$  Al foil with a doctor blade. The wet coating was dried on a hotplate at  $80\ ^\circ\text{C}$ . Rectangular cathodes ( $23\ \text{mm} \times 18\ \text{mm}$ ) were cut out and pressed several times in a roll press to obtain net electrode thickness of approximately  $35\ \mu\text{m}$ . The electrodes were then dried at  $110\ ^\circ\text{C}$  for 12 h in vacuum to remove any adsorbed water and transferred into an argon-filled glovebox, where pouch cells with pure metallic lithium as anode and 1 M  $\text{LiPF}_6$  in 1:1 fluoroethylene carbonate/diethyl carbonate (FEC/DEC) as electrolyte were assembled. Each cell was cycled between 2.0 and 4.8 V with a current of  $15\ \text{mA g}^{-1}\text{LMO-NCM}$ . Cells were charged to certain capacities in the first and in the second charge: the equivalent of 1st cycle irreversible capacity, 100 mAh, 150 mAh, 200 mAh, 250 mAh and 300 mAh per gram active material. Each charged cell was disassembled and the cathode was thoroughly washed with dimethyl carbonate (DMC; anhydrous,  $\geq 99\%$ , Sigma-Aldrich) and dried under vacuum for 12 h.

Charged, washed, and dried cathode materials were scratched off from the Al current collector, sealed into  $100\ \mu\text{l}$  Al crucibles by cold welding and thus prepared for thermal analysis. TGA and DSC were done simultaneously by MettlerToledo STARE TGA/DSC1 thermal analyzer. Crucible lid was pierced by the sampling robot before analysis in order to allow evolved gases to escape. Thermal analysis was conducted between  $25\ ^\circ\text{C}$  and  $600\ ^\circ\text{C}$  at a scan rate of  $5\ \text{K min}^{-1}$  under a flow of argon ( $50\ \text{ml min}^{-1}$ ). After thermal analysis, samples were cooled down to  $25\ ^\circ\text{C}$  in the inert atmosphere under the same flow of argon.

For comparison, cathodes with same composition were prepared from NCM and LCO (both from Enax, Japan) as active materials. NCM cathodes were built into half-cells vs. Li using same electrolyte as for LMO–NCM and cycled between 2.75 and 4.8 V. NCM cathodes charged in both the first and second cycles were investigated to compare their cycling history dependence of thermal stability with that of LMO–NCM cathodes. LCO cathodes were built in half-cells vs. Li using 1 M  $\text{LiPF}_6$  in 1:1 ethylene carbonate/diethyl carbonate (EC/DEC) as electrolyte and cycled between 3.0 and 4.2 V. Here the results of LCO cathode charged to  $137\ \text{mAh g}^{-1}$  in the second cycle are reported. The same protocol of sample preparation was kept throughout for thermal analysis investigation.

All specific capacities in this paper are absolute. This means that the values refer to the cumulative capacity of the electrodes, i.e. the difference between total charge and discharge capacities starting from the beginning of cycling. We have assumed that no side reaction takes place during the charge–discharge process, so each electron passing the circuit is due to one lithium ion movement between the electrodes.

In order to investigate structural changes in the active material during charge/discharge and decomposition, powder X-ray diffraction (XRD) analysis was done by Rigaku SmartLab XRD in the range of  $15^\circ < 2\theta < 70^\circ$  with Cu-K $\alpha$  radiation ( $U = 45\ \text{kV}$ ,  $I = 100\ \text{mA}$ ). XRD

measurements were repeated on the same samples before and after thermal treatment by TGA/DSC.

## 3. Results and discussion

### 3.1. Electrochemical characterization

Fig. 1 shows a characteristic cycling profile of the LMO–NCM cathode. During the first charge, the characteristic profile with two charging regions is observed. The first region below 4.4 V gives a charge capacity of about  $154\ \text{mAh g}^{-1}$  (0.5 mol of Li removal), which is attributed to Li extraction from NCM component. The second region with a flat plateau at 4.5 V corresponds to the activation of LMO component. An overall charge capacity of  $310\ \text{mAh g}^{-1}$  was achieved. During discharge, Li is inserted back into the lattice, in both the NCM component (at higher voltage) and the LMO component (at lower voltage). The first cycle discharge capacity was  $255\ \text{mAh g}^{-1}$  with an irreversible capacity of  $55\ \text{mAh g}^{-1}$ . Multiple cells were made and charged and discharged to different states of charge (represented by squares in Fig. 1) for thermal stability tests. The cathode at different states of charge ( $\text{Li}_{1.167-x}\text{Mn}_{0.5}\text{Ni}_{0.167}\text{Co}_{0.167}\text{O}_2-y$ ) from each cell was removed for the analysis. One should note that the electrodes with the same cumulative capacity (same amount of Li in the material) during the first and second charges have vastly different electrode potentials. This is unique for LMO–NCM and is not the case for LCO and NCM. This is due to the difference in the structure of the LMO–NCM material before and after LMO activation. Take for example samples (A) and (B) at a cumulative capacity of  $150\ \text{mAh g}^{-1}$  during the first charge and second charge ( $x \sim 0.5$ ), as indicated in Fig. 1. The open circuit potentials for the electrodes are 4.37 V and 3.28 V, respectively. Sample (A) has undergone first charging with Li removal only from the NCM component in the structure. The oxidation states of Ni, Co and Mn are in principle 4+. On the other hand, sample (B) has undergone LMO activation during first charge. Most of the charge–discharge capacity originates from oxidation state change of Mn below a potential of 3.8 V, and Ni and Co above 3.8 V. We expect sample (B) to have oxidation states of Ni and Co of close to 2+ and 3+, with a mixed oxidation state of Mn between 3+ and 4+. A comparison between the first and second cycles can therefore give us information on how the stability of the material is affected by the mechanism of LMO activation and the oxidation states of the transition metals in the material.

### 3.2. Thermal analysis

Fig. 2 shows TGA curves of the LMO–NCM cathodes in Ar at different states of charge. Dotted lines correspond to electrodes from the first

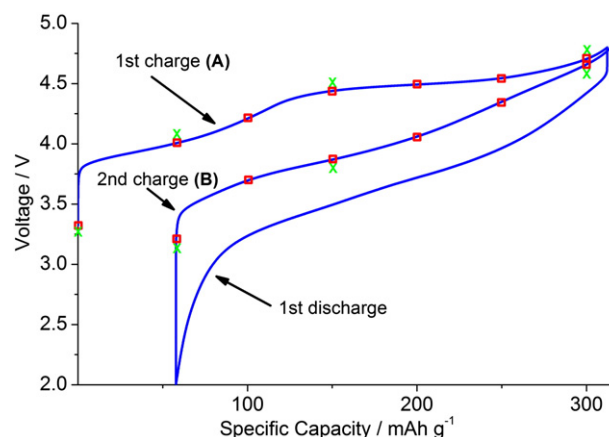


Fig. 1. Cycling profile of cathode vs Li between 2 and 4.8 V at a current of  $15\ \text{mA g}^{-1}$ . Squares indicate at which points cathodes were removed from the cells, washed, dried and analyzed by TGA/DSC. Crosses indicate at which points XRD spectra were taken for washed and dried cathodes, as well as thermally decomposed (after TGA/DSC) cathodes.

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